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Solution for removing side-wall residue after dry etching - comprising fluorine-contg. cpd., sulphuric acid and hydrogen peroxide

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Abstract (Basic): TW 296405 A

A soln. for removing side-wall residue after dry etching of polysilicon or non-metallic cpd. of silicon comprising H2SO4, H2O2 and fluorine-contg. cpd., where the wt. ratio of H2O2 to H2SO4 is from 1:5-1:20, the wt. ratio of H2SO4 to fluorine-contg. cpd. is from 300:1-500:1, and the fluorine-contg. cpd. is selected from the cpds. formed by fluorine ion and single valent cation, the single valent cation being selected from free alkaline metal cation, ammonium ion and hydrogen ion.

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Title Terms: SOLUTION; REMOVE; SIDE; WALL; RESIDUE; AFTER; DRY; ETCH; COMPRISE; FLUORINE; CONTAIN; COMPOUND; SULPHURIC; ACID; HYDROGEN; PEROXIDE
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Title: SOLUTIONS AND PROCESSES FOR REMOVAL OF RESIDUE AFTER DRY ETCHING

Abstract: The present invention relates to a novel process for removing sidewall residue after dry etching. Conventionally, after dry etching, photoresist and sidewall residue are removed by ozone ashing and hot sulfuric acid. Normally, they are hard to be removed completely. It was found in the present invention that the addition of fluorine-containing compound, preferably hydrogen fluoride and ammonium fluoride, in sulfuric acid results in complete removal of photoresist and sidewall residue without the need for stripper. The process is simple and does not affect the original procedures or the other films present. The present invention also relates to a novel solution for removing sidewall residue after dry etching, which comprises sulfuric acid and a fluoride-containing compound, in the range of from 10:1 to 1000:1 by weight.

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Background of the invention

1. The field of the invention

The present invention relates to a novel solution used in the process of integrated circuit dry etching. More particularly, the present invention relates to a novel solution for removing sidewall residue after dry etching and a novel process for removal of sidewall residue by using the solution.

2. Prior arts

Processes of integrated circuit manufacturing are as follows: First is depositing a conductive metal, such as Al, on a substrate, such as a wafer, then coating a photoresist layer. Second, printing the circuit patterns, which are desired as a positive photoresist or negative photoresist on the photoresist; then being exposed to radiation so as to activate the photoresist layer which should be exposed to, that makes exposed and unexposed areas with different solubilities in developer solution. And processing the activated photoresist layer by developer solution to remove the soluble area of the photoresist layer, so that the substrate surface can be revealed and desired circuit pattern can be added on it. This process is achieved by penetrating conductive metals or metal oxides, or by boron implantation, or by removing the soluble areas in order to reveal the conduction layer, and it can be removed by etching except for all the other parts of desired circuit pattern.

Photoresist layer can be "positive photoresist", the exposure area in developer solution become soluble; or can be "negative photoresist", the exposure area in developer solution become insoluble. Positive photoresist includes proper resin, such

as novolac resin, melamine formaldehyde resin, acrylic ester or methyl acrylic resin, polyvinyl cinnmate or crosslink resin while negative photoresist includes such as polyisoprene. Generally, photoresist will be baked under high temperature to ensure crosslink after being developed.

After creating desired IC pattern on the substrate, if more sophisticated IC pattern is to be processed, the sidewall residue must be removed with high-valued efficiency. That's why photoresist stripper is used, as US Patent No. 4,963,342 mentioned.

In the etching process of VLSI □Very Large Scale Integrated□or ULSI□Ultra Large Scale Integrated□, sidewall passivation formed after dry etching usually used to achieve anisotropic of etching process, as descirbed in J. L. Vossen, et al, J. Vac. Sci. Techniool. Al, 1453□1983□; J. H.. Thomas, et al, Appl. Phys. Lett. 43,859□1983□; D. Thomson, et al, Appl. Phys. Lett. 146,1103□1985□; and J. M. E. Harper, et al, J. Electrochem. Soc. 128,1077□1981□. While etching Poly-Si, according to etching chemistry of chlorine or bromohydride, mostly oxygen is added to enhance the anisotropic tendency and selectivity to oxide layer, as J.Morimoto. et al, Digest of papers. Microprocess 202□1992□described. When using chorine gas as etching gas to etch polysilicon, the products will be silicon chloride. If oxygen exists, silicon chloride will be oxidized to silicon oxide, as K. V. Guinn, et al, J. Vac. Sci. Technol. B 13,214 □1995□described. This silicon oxide is so-called sidewall passivation, preventing materials from isotropic etching. The sidewall passivation formed after dry etching process cannot be removed completely by conventional ozone ashing and hot sulfuric acid process, because the sidewall passivation is silicon oxide, hence it can't be removed by using sulfuric acid. The general process may immerse it in dilute

hydrofluoric acid after the treatment of ozone ashing and hot sulfuric acid, and must be very quick so as not to attack bottom oxide layer. Or using stripper, however, it is less convenient. Hence, the process of removing sidewall residue after dry etching should be improved.

Summary of the Invention

The present invention relates to a novel solution formed after adding fluoride-containing compound, preferably hydrofluoric acid and ammonium fluoride, into the sulfuric acid. This solution can completely remove sidewall residue formed after dry etching.

The invention also relates to a novel process removing sidewall residue formed after dry etching by above-mentioned solution.

Brief Description of the Drawings

Fig. 1 shows the flow chart of the conventional photoresist stripping process and the novel photoresist stripping process in the IC manufacturing process.

Fig. 2 shows the magnified picture of the wafer treated with the conventional photoresist stripping process. Magnification is 11,000 times.

Fig. 3 shows the magnified picture of the wafer treated with the novel photoresist stripping process. Magnification is 11,000 times.

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Detailed Description of the Invention

In the process of manufacturing integrated circuit, wafer surface is cleaned before film growing, then SiO_2 and polysilicon film are deposited on it. After that, the processes are photoresist coating, exposure, developing, etching and photoresist stripping as shown in Fig. 1. Conventionally, photoresist stripping process is treated by ozone ashing and hot sulfuric acid, and this process cannot completely remove sidewall residue formed after dry etching, as Fig. 2 shows. Following immersion into diluted hydrofluoric acid solution or stripper is required. The present invention is a process when boiling sulfuric acid after ozone ashing, adds fluoride-containing compound into sulfuric acid and controls the ratio of sulfuric acid to fluorine-containing compound so as to remove the sidewall residue formed after dry etching completely, as shown in Fig. 3. This process is simple, no need for additional steps, reducing to only one step. Fig. 1 shows the flow chart of the process.

This invention uses a novel solution to remove sidewall residue formed after dry etching, which comprises sulfuric acid and a fluoride-containing compound, in the range from 10:1 to 1000:1 by weight, preferably in the range of 100:1 to 700:1, more preferably in the range of 300:1 to 500:1.

The fluoride-containing compound can be any compound containing fluoride, preferably composed of fluorine ion and mono-charge cation, such as alkaline metal cation, ammonium cation and hydrogen ion, more preferably hydrofluoric acid and ammonium fluoride. The novel solution is prepared by adding proper ratio of hydrofluoric acid or ammonium fluoride into sulfuric acid, and then add hydrogen peroxide when mixing, at temperature 100-140°C, preferably at 120 °C. The above

mentioned chemicals are commercially available, such as H_2SO_4 96%, H_2O_2 31%, HF 49%, NH_4F 40%.

When using this new process to remove sidewall residual after dry etching, not only organic compounds can be removed but also inorganic ones such as SiO_2. It can be implemented without increasing difficulty of the process. Only when removing photoresist and sidewall residual after dry etching, soak ozone ashing wafer in the pre-mixed solution of sulfuric acid and fluorine-containing compound, and maintaining operation pressure at 1 atm, temperature at 100-140 °C□preferably at 120 °C□for 10 minutes. The photoresist and sidewall passivation formed after dry etching can be removed completely without any influence on the film of Poly-Si; it only slightly etches bottom oxide layer□SiO_2□, less than 1 Å/min. After dry-etching process, the operation of ozone ashing is put the wafer into reaction chamber with oxygen and oxygen atoms both decomposed from ozone. Because photoresist contains large amount of carbon atoms, which form CO_2 under high temperature condition, so one can know whether ozone ashing reaction completes or not by detecting the amount of CO_2.

The new process is simple, speedy, and without any stripper or other solutions. It costs less, with high feasibility and practicability. The process is suitable for several kinds of photoresists including g-line, I-line, deep UV, E-beam and X-ray resist.

The following examples are further explanation for the invention but the scope of the invention is not limited. All possible substitutes and adjustments done by those who are familiar with this technique belong to the spirit and scope of this invention.

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Example 1

The photoresist used in the process is FH-6400 g-line photoresist, produced by Japan FUJI-HUNT. Exposure is done by PAS2500/10 g-line stepper, produced by Netherlands ASM Co. The process uses FHD-5 developer, containing TMAH 2.38%, produced by FUJI-HUNT. Developing time is 60 sec. The ECR□Electron Cyclotron Resonance□ etching machine is used for etching 3000Å of Poly-Si. The plasma is produced by using Cl_2 □95sccm□, O_2□5sccm□and 250W microwave. 35W of RF provides DC Bias. Pressure in the chamber is 3 mTorr while temperature is –20°C. Etching time is 70 sec. The etching rate is 2612Å/min for Poly-Si, 26Å/min for SiO_2, 766Å/min for photoresist. As for selectivity, the ratio of Poly-Si to SiO_2 is 100 □2612/26□, while Poly-Si to photoresist is 3.4□2612/766□. □sccm = standard cubic centimeter per minute□

Comparative Example

After etching, the conventional process is used to remove photoresist. First, the photoresist is removed by ozone ashing, the condition of ozone ashing is one wafer per time at temperature 200 to 300°C. At this temperature, decomposed oxygen from O_3 reacts with carbon of photoresist and forms CO_2, which takes one minute on average to react completely. Then the wafer is immersed in mixed solution of sulfuric acid and hydrogen peroxide at 120°C for 10 minutes. The magnified picture of treated wafer is shown in Fig. 2. At this stage, only photoresist can be removed while sidewall passivation residues after etching cannot be removed completely. Diluted hydrofluoric acid or stripper is needed for further treatment.

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Example 2

After etching, present novel process is used to remove photoresist. First, the photoresist is removed by ozone ashing treated in the same way as the comparative example. Then, the wafer is immersed in the mixed solution of sulfuric acid, hydrofluoric acid and hydrogen peroxide at 120°C for 10 minutes. The ratio of sulfuric acid + hydrofluoric acid to hydrogen peroxide is 3:1 by volume. The magnified picture of treated wafer is shown in Fig. 3. It is obvious that photoresist and sidewall passivation after etching are completely removed by this single step without affecting Poly-Si and bottom SiO_2 layer.

Example 3

After etching, present novel process is used to remove photoresist. First, the photoresist is removed by ozone ashing treated in the same way as comparative example. Then the wafer is immersed in the mixed solution of sulfuric acid, ammonium fluoride and hydrogen peroxide at 120°C for 10 minutes. The ratio of sulfuric acid + ammonium fluoride to hydrogen peroxide is 3:1 by volume. Referring to the magnified picture of treated wafer, it is obvious that photoresist and sidewall passivation after etching are completely removed without affecting Poly-Si and bottom SiO_2 layer.

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Claims

1. A solution for removing Poly-Si or sidewall residue of non-metal compound of Si after dry etching, which comprises sulfuric acid, hydrogen peroxide and fluorine-containing compound, wherein a ratio of hydrogen peroxide to sulfuric acid is in the range of 1:5 to 1:20 by weight, and a ratio of sulfuric acid to fluorine-containing compound in the range of 300:1 to 500:1 by weight, and the fluorine-containing compound is composed of fluorine ion and mono-charge cation selected from one of the group consisting of alkaline metal cation, ammonium cation and hydrogen ion.

2. The solution according to claim 1, wherein the fluorine-containing compound is hydrofluoric acid.

3. The solution according to claim 1, wherein the fluorine-containing compound is ammonium fluoride.

4. A process for removing sidewall residue after dry etching at temperature in the range of 100 to 140°C, using the solution according to claim 1.

5. The process according to claim 4, wherein the fluorine-containing compound is hydrofluoric acid.

6. The process according to claim 4, wherein the fluorine-containing compound is ammonium fluoride.